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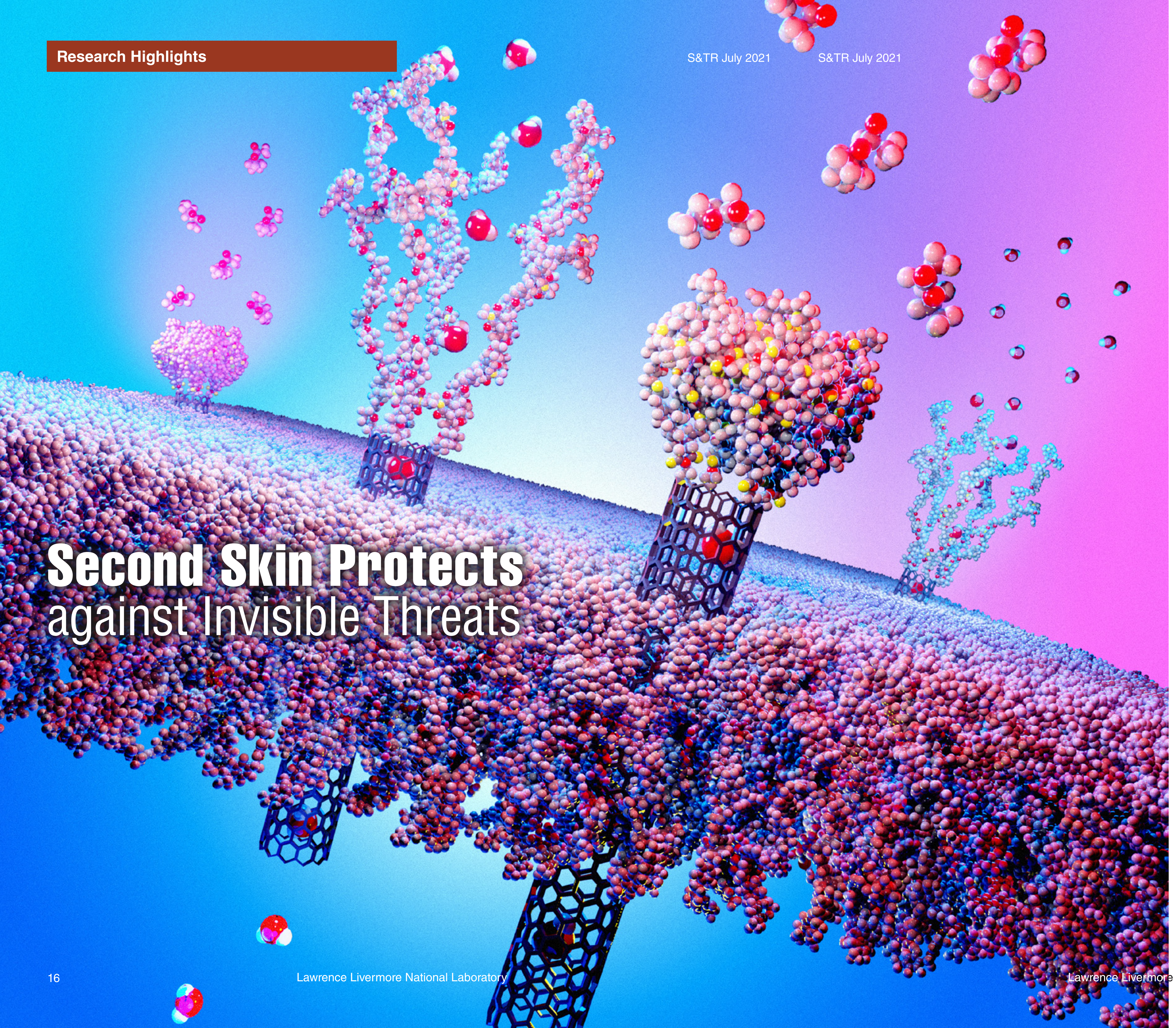
Second Skin Protects against Invisible Threats



FIRST responders, medical personnel, and soldiers on the frontlines of conflicts and emergencies prepare to encounter conventional weapons, but often they are not adequately equipped to face invisible threats from chemical and biological agents while executing their jobs. Sarin and chlorine gas have been used recently in the Syrian conflict, and the COVID pandemic has shown that protection against viruses is an urgent need. To help protect frontline workers against chemical and biological weapons, the Defense Threat Reduction Agency (DTRA) has been funding a Laboratory team and its collaborators to develop "smart" materials for uniforms that can shield against these threats. As the Laboratory continues work on the second phase of this project, called the Dynamic Multifunctional Materials for a Second Skin "D[MS]^2" program, researchers are building on the successes of the first phase of their work to make the material elastic and resistant to biological, blister, and nerve agents. The "second skin" material is made up of two layers. The first layer, consisting of carbon nanotubes (CNTs) embedded in a polymer matrix, blocks biological agents, and the second threat-responsive polymer layer blocks nerve and blister agents.

Most importantly, this innovative two-layer material can breathe and is comfortable to wear even over long use. Traditional military uniforms designed to block chemical weapons are passive systems based on impermeable barriers or adsorptive laminates, but they are heavy and stiflingly hot. They hinder the body's ability to cool itself. Wearers risk heat stress, especially if they are performing strenuous work in hot environments potentially contaminated with nerve, blister, or biological agents. So far, first responders and military personnel have had to sacrifice comfort for protection from biological and chemical hazards; however, the new second skin materials are porous and rapidly wick water vapor (sweat) away from the skin while still protecting against threats.

Building the Base Layer

Lawrence Livermore researchers built the base layer out of trillions of CNT pores, which are so small that bacteria and even viruses cannot pass through them. The base layer consists of a membrane of vertically aligned CNTs with a diameter less than 5 nanometers, which is 5,000 times thinner than a human hair. The CNTs are vertically "grown" in a tightly packed forest,

This rendering shows the carbon nanotubes (CNTs) embedded in a polymer matrix and functionalized with responsive polymers. In a safe environment, the membrane "breathes," and the water vapor (below) can flow easily through the CNTs and past the responsive polymer chains at their ends. If an environmental threat exists, the polymer chains collapse, preventing chemical agents from entering the pores. (Image by Ryan Chen.)

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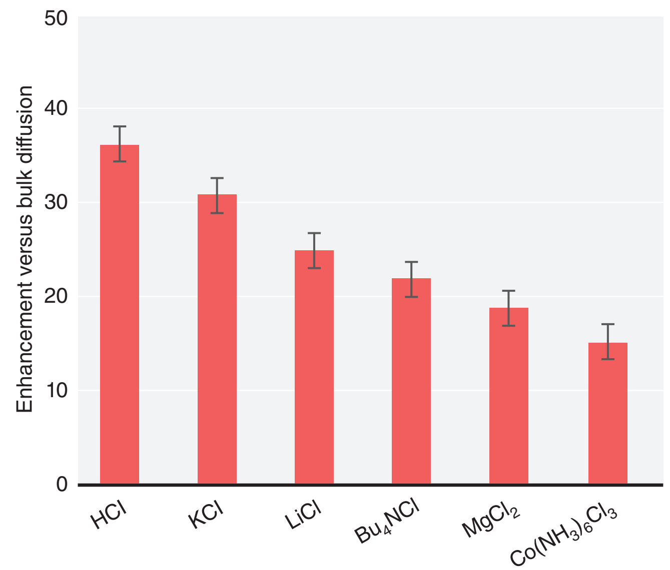
and the gaps between the nanotubes are filled with a polymer to prevent leakage. Water molecules can easily pass through the CNTs at a rate greater than other commercially available breathable materials and more than an order of magnitude faster than predicted by gas diffusion theories. (See *S&TR*, December 2016, pp. 20–23.)

"When testing our dynamically responsive membranes, there were some unexpected results. Because of the intrinsic smoothness of the pore walls, CNTs have exceptionally fast gas and liquid flow. Counterintuitively, the flow per pore gets even faster as the tubes get smaller, and we found that the overall membrane breathability increases even as the diameter of the CNTs decreases," said Francesco Fornasiero, Livermore's leader of the multi-institutional team of researchers. "In other tests, we found that small ions such as potassium, chloride, and sodium, which are exuded in perspiration, also permeated through CNTs much faster than expected."

Threat-Responsive Polymer Layer

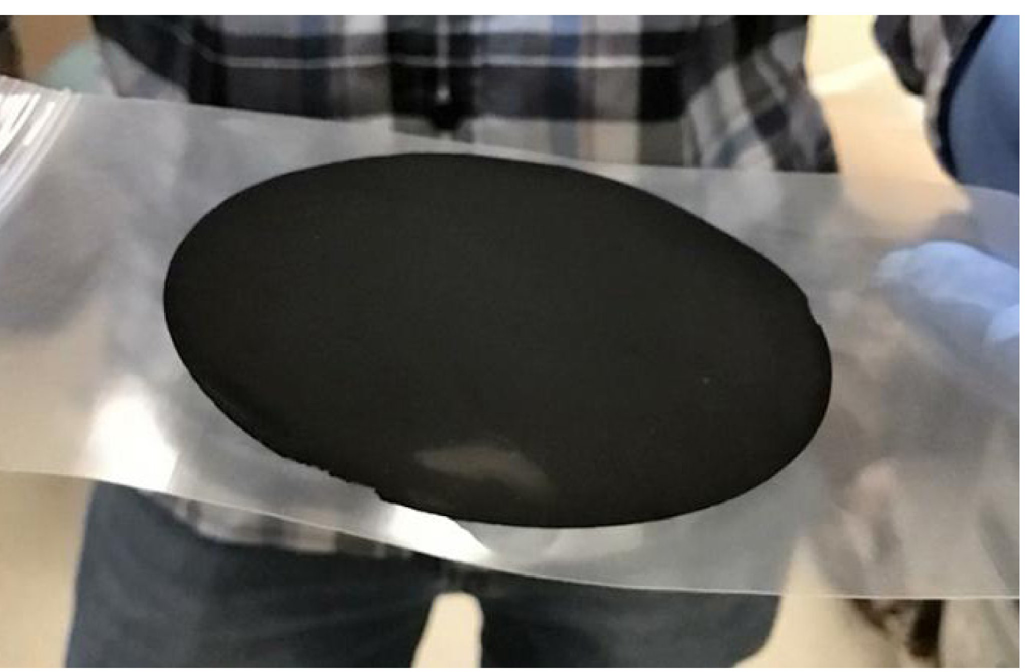
Unlike biological agents, chemical agents are too small to be blocked by CNTs, so the team developed a second "smart" layer that can protect against nerve agents only when protection is needed. They are also working on expanding that protection to address blister agents. This ultrathin, threat-responsive polymer layer is grown on the surface of the base membrane with polymer chains extending outward from the CNT composite surface. If a nerve agent comes into contact, these chains immediately collapse, temporarily blocking the pores, but this effect can be reversed by treating the material with a base, effectively decontaminating the suit, and possibly allowing its reuse.



Salt diffusion rates inside CNTs are more than one order of magnitude faster than in bulk aqueous solutions.

One of the most remarkable features of the material is that the protective response is localized, blocking permeation of the threat only in the contaminated area, while other parts of the uniform remain breathable. Another important feature is that the material automatically provides protection even if the wearer is unaware that a threat is present.

After developing the Phase I materials, DTRA asked if Livermore could make the membrane more comfortable to wear. By eliminating pockets of air between the uniform and the wearer's skin, stretchable materials reduce a large fraction of the uniform's thermal resistance or temperature difference between the material's two sides. To accomplish this, the team changed how the material is fabricated, and work continues to demonstrate that this elastic second skin maintains the same level of breathability and protection of the Phase I membranes.



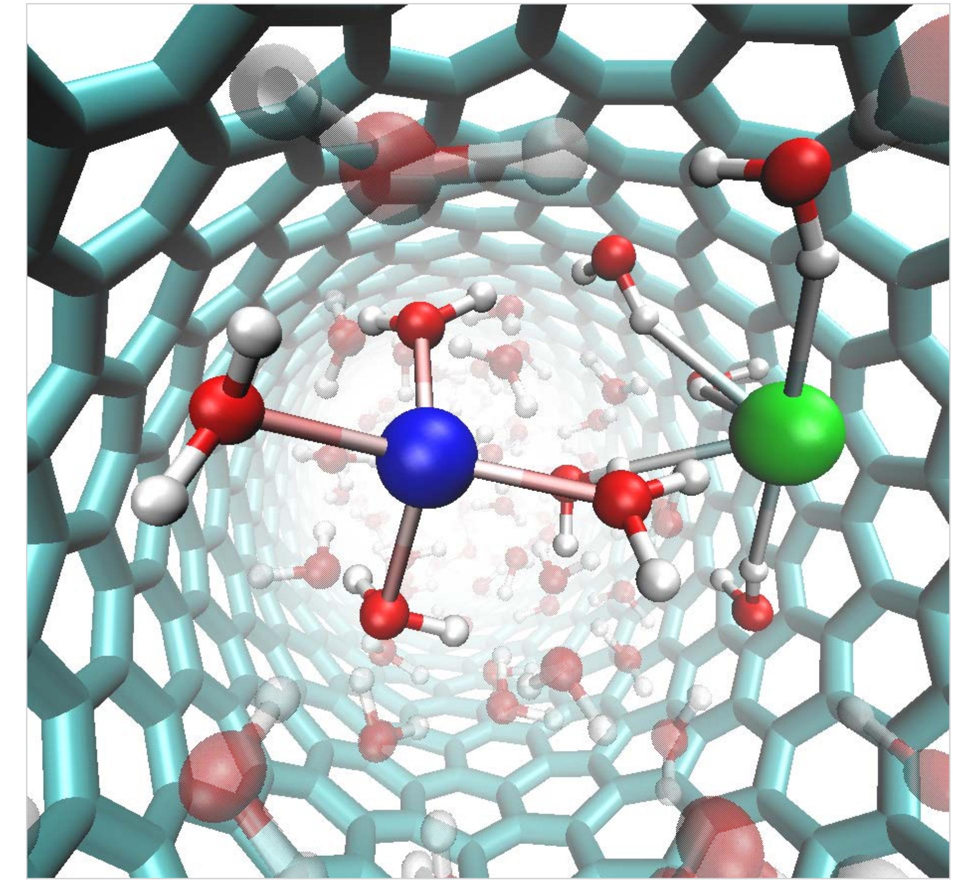
This membrane, also known as "second skin" for its protective properties, is made of vertically aligned, single-walled CNTs embedded in a polymer matrix, and could provide the protective layer of a first-responder uniform.

While addressing Phase II goals, the team is looking ahead to Phase III, which involves scaling up the process for material production and improved manufacturability. The current process will need to be streamlined before the material can be produced in large volumes, and the team is exploring options for continuous, scalable fabrication techniques. Collaborators at the U.S. Army Combat Capabilities Development Command Soldier Center and Edgewood Chemical Biological Center will help with the suit design and material properties evaluation, including their protection level.

Need for Similar Materials in Other Applications

As the team members continue working on the material for first responder and soldier uniforms, they have also conducted some preliminary tests for other applications that need the unique transport properties of CNTs. A first, obvious application is for breathable and comfortable medical scrubs for doctors and nurses, who regularly deal with biological threats, as well as sheets and hospital gowns for patients.

In another medical application, CNT membranes could enable significantly shorter treatment time for hemodialysis patients, thereby greatly improving their quality of life. CNT membranes are expected to allow small molecules like salt, urea, and other waste products in the bloodstream to pass through much more rapidly than conventional dialysis membranes, while retaining the larger and valuable components such as proteins and red blood cells. CNTs could also be used to separate macromolecules—proteins, DNA, and polysaccharides, for example from smaller components used during their synthesis, modifications, or labeling that need to be removed from the final product. Other potential applications include recovery of pharmaceuticals used during synthesis, water purification, desalination of dilute solutions, and wastewater treatment. For example, in one recent experiment, the team used CNTs to remove dilute dyes from concentrated salt solutions. This process could allow the dye industry to reclaim and potentially reuse dye, converting a waste stream into useful feedstock. Furthermore, membranes with CNT pores provided superior filtration and separation when compared to other state-of-the-art products with similar pore sizes.



Small ions permeate through the inner volume of nanometer-wide CNTs in this artistic rendering of single-walled CNTs (above). The ions permeate at rates that surpass diffusion in bulk water by an order of magnitude. (Image by Tuan Anh Pham.)

The Laboratory has been building expertise in novel uses of the unique transport properties of CNTs over many years. The second skin team has drawn on a diverse skill set found across the Laboratory, from materials science and nanotechnology to physics, polymer science, and computational modeling. Ongoing work with collaborators at Massachusetts Institute of Technology, Rutgers University, and Chasm Advanced Materials continues to help push the boundaries of this technology area.

—*Karen Rath*

Key Words: biological agent, breathability, carbon nanotube (CNT), chemical agent, first responder, ion permeation, membrane, nerve agent, polymer matrix, second skin, soldier, uniform.

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